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Enhancement of esterification conversion using pervaporation membrane reactor

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Abstract

In the present study, the esterification reaction of propionic acid with isobutyl alcohol to produce isobutyl propionate and water was studied. The performance of esterification reaction was compared by using the batch process and the pervaporation assisted hybrid process which performs the reaction and separation simultaneously. A polyvinyl alcohol–polyethersulphone (PVA–PES) hydrophilic polymeric membrane was used in the study to separate water and also to shift the equilibrium. The influence of process parameters such as catalyst loading, molar ratio of acid to alcohol, reaction temperature and ratio of membrane area to initial reaction volume (S/V) was studied. The results showed that the pervaporation assisted esterification process gave more conversion than the batch process of esterification. The membrane showed high selectivity to the removal of water in the propionic acid, isobutyl alcohol, isobutyl propionate and water mixture. Moreover, the conversion of propionic acid was enhanced by enhancing the catalyst amount, molar ratio of acid to alcohol, reaction temperature and S/V ratio.

Keywords: Pervaporation; PVA–PES; Hydrophilic membrane; Esterification; Isobutyl propionate

1. Introduction

In recent years, the processes which work efficiently with low energy consumption have become a great deal of interest in various chemical industries. Particularly, a hybrid process involving the reaction and separation together has been often used to enhance the efficacy of the esterification process. In this regard, the pervaporation membrane reactor has gained great interest due to its ability to incorporate the reaction and separation of one or more species into a single unit [1–3]. Pervaporation involves the selective removal of the product immediately after it is formed and therefore, efficiently shifting the reaction to the product side in contrast to the traditional process of reactive distillation [4,5].

Generally, esterification reactions are limited by thermodynamic equilibrium. It produces water as a byproduct which reduces the forward reaction rate. Thus, the esterification reactions performed in batch reactors encounter low conversions due to the problems imposed by thermodynamics of the reaction [6]. Pervaporation is one of the most promising approaches to enhance the conversion of esterification reaction due to its ability of selective removal of water from the reaction mixture with lower energy requirements [7]. The combination of a pervaporation process with conventional batch esterification process is attractive because it offers the opportunity to continuously shift the equlibrium towards the ester production beyond the thermodynamic equilibrium by removing water from the reaction mixture [8]. Pervaporation has been recognized as a successful technique for selective removal of certain components from a liquid mixture because of its ability to separate azeotropic mixtures. Pervaporation also has an advantage of separating azeotropic, heat sensitive and close-boiling mixtures due to its mild operating conditions with zero emission to the environment and no requirement of additional species into the feed stream. Several studies [7,9–11] demonstrate the application of pervaporation by using a hydrophilic membrane to remove water and thereby increasing the ester yield.

Isobutyl propinate is a clear colourless liquid with characteristic fruity odour reminiscent of apricot, apple and cherry. Due to this, it is widely used in wine industries to impart flavour to various products. The pervaporation assisted esterification of

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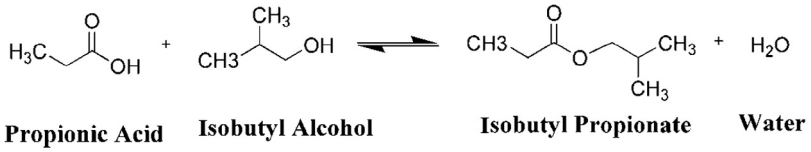

Scheme 1. General mechanism of esterification of propionic acid with isobutyl alcohol.

few acids with alcohols has been reported in the literature [12–16]. However, esterification coupled with pervaporation of propionic acid and isobutyl alcohol using *p*-toluene sulphonic acid as catalyst was not investigated until now. In this study, the batch process and the pervaporation assisted hybrid process of esterification of propionic acid with isobutyl alcohol producing isobutyl propionate and water were studied and compared. The pervaporation coupled experiments were performed using the polymeric hydrophilic membrane, polyvinyl alcohol–polyethersulphone (PVA–PES). *p*-Toluene sulphonic acid (*p*-TSA) was used as a catalyst for the esterification reaction. The effects of various process parameters namely, catalyst loading, initial molar ratio of acid to alcohol, reaction temperature and ratio of effective membrane area to initial reaction volume (S/V) were investigated. To study the effect of each parameter, the catalyst loading was varied from 1% to 3% wt/wt, molar ratio of acid to alcohol was varied between 1:1 and 1:2 by varying the reaction temperature from 343 to 363 K for both batch process and pervaporation assisted hybrid process. The effects of these reaction parameters were studied individually in both processes and compared with each other. Moreover, the S/V ratio which is the most significant parameter in the pervaporation was investigated at 51.66 m^{-1}, 38.75 m^{-1} and 31 m^{-1} for pervaporation assisted hybrid process. The general mechanism of esterification reaction of propionic acid with isobutyl alcohol to produce isobutyl propionate and water can be represented as Scheme 1.

2. Materials and methods

2.1. Membrane

A commercial polymeric hydrophilic PVA–PES composite membrane procured from Permionics Membranes Pvt. Ltd., India was used in the pervaporation study. The membrane was selective for the removal of water. The thickness of the membrane was 250 μm with effective membrane area of 0.0155 m^2.

2.2. Chemicals

All chemicals were of analytical grade. Propionic acid (Merck, purity > 99%) and iso-butyl alcohol (Merck, purity > 99%) were used as reactant. *p*-Toluene sulphonic acid (Fisher Scientific, purity > 99%) was used as catalyst for the esterification reaction. Double distilled water was used for the preparation of solutions required for analysis of the product.

2.3. Batch experiments

The schematic representation for the batch set-up for the esterification is shown in Fig. 1. The set-up consists of a three neck borosil glass reactor (1 L capacity) equipped with a condenser. The temperature inside the reactor was maintained within accuracy of ±0.5 °C by using PID temperature controller. The magnetic stirrer was placed inside the reactor for complete mixing of the reaction mixture. First, the isobutyl alcohol was charged into the reactor and heated under reflux up to a desired set-point temperature. Once the set-point temperature was reached, the prehated propionic acid at the same temperature was added to the reactor followed by the addition of catalyst. This time was taken as zero time of reaction and the reaction was continued up to a fixed reaction time of 8 h. The aliquots of sample were withdrawn at definate intervals and analysed by the method of titration using 0.1 N NaOH with phenolphthalien as indicator. Subsequently, the moisture content in the reaction mixture was determined by Microprocessor based Karl Fisher Titrator (Bio-Technics, India).

2.4. Pervaporation set-up

The ex-situ type pervaporation (PV) membrane reactor set-up supplied by Permionics Membranes Pvt. Ltd., India was used for pervaporation assisted esterification reaction. The schematic representation is shown in Fig. 2. The PV set-up composed of pervaporation module coupled with the batch set-up. The PVA–PES membrane was sealed in the middle of the pervaporation module with effective membrane area of 0.0155 m^2.

2.5. Pervaporation experiments

In order to study the performance of esterification by pervaporation, the similar reaction procedure as dicussed in Section 2.3 was incorporated by employing ex-situ pervaporation membrane reactor. The feed reactor was heated up to a desired temperature until the steady state was reached. A peristaltic feed pump was used to circulate the feed to the pervaporation module and recycled back to the feed reactor. A vacuum pressure of 160 mm Hg was applied with the help of a vacuum pump to the permeate side. The water vapours separated by the membrane in the pervaporation module were condensed by using the chiller which was maintained at the temperature of −5 °C. The vapours in the permeate side were collected, weighed and analysed.

3. Results and discussion

The experiments with similar operating conditions were conducted for both batch (without PV) and pervaporation (with PV) experiments. In batch esterification, mainly three operating parameters namely catalyst loading, molar ratio of acid to alcohol and reaction temperature were directly affecting the esterification process. However, in esterification coupled with

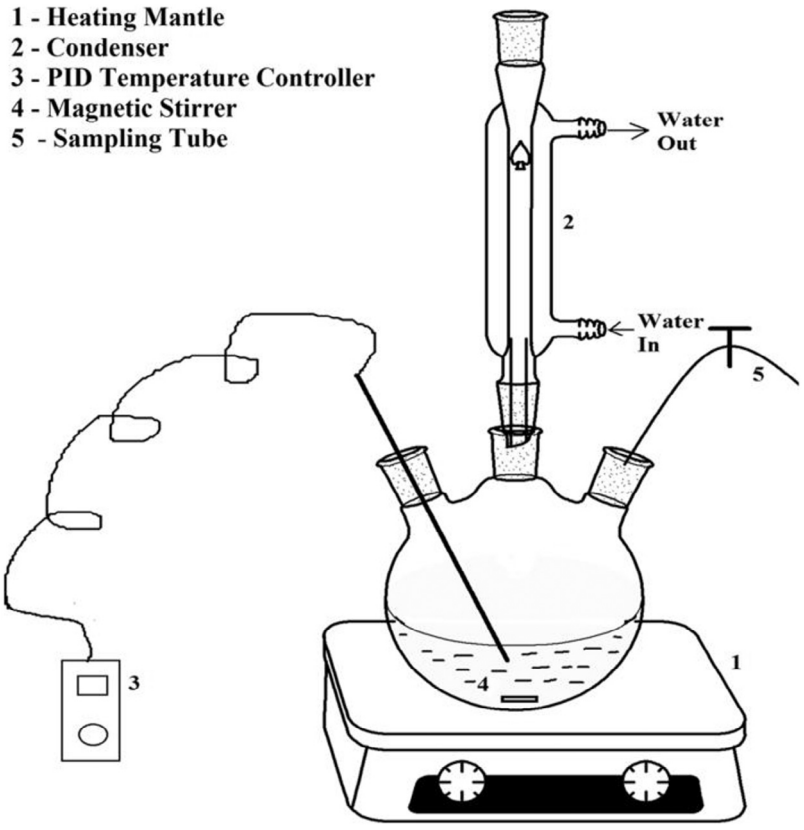

Fig. 1. Set-up for batch experiments for the esterification reaction (without PV).

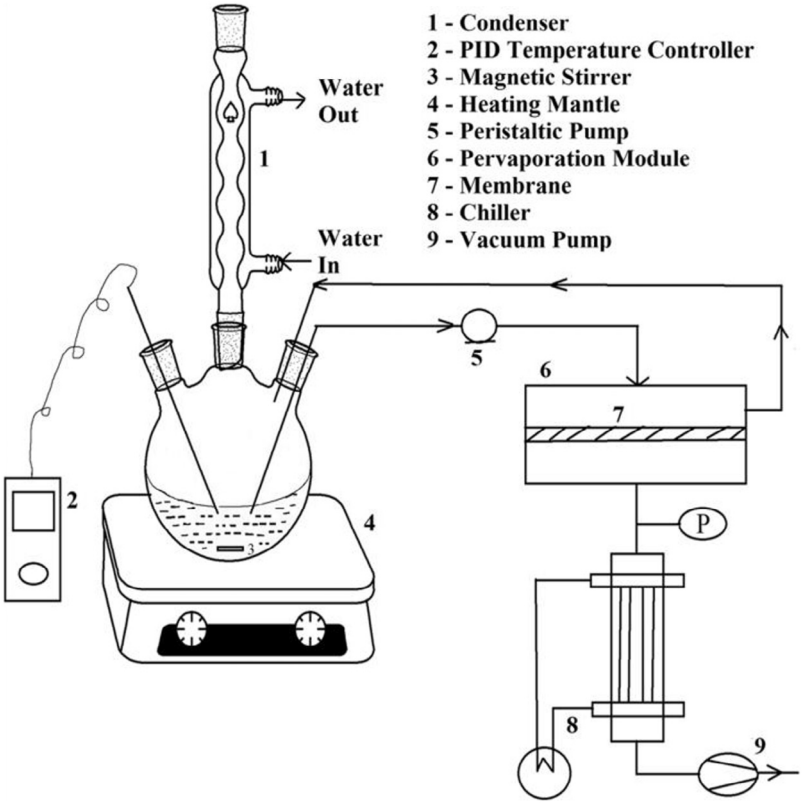

Fig. 2. Pervaporation membrane reactor set-up for the esterification reaction (with PV).

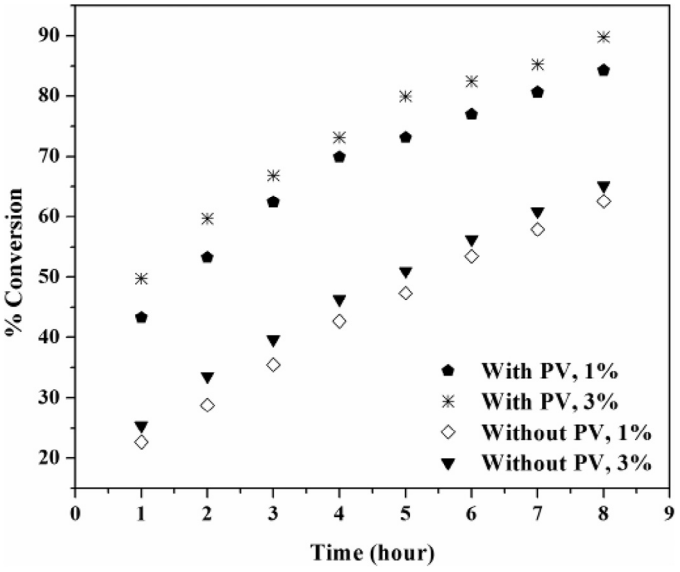

Fig. 3. Effect of catalyst loading on the conversion of propionic acid for the esterification with PV and without PV.

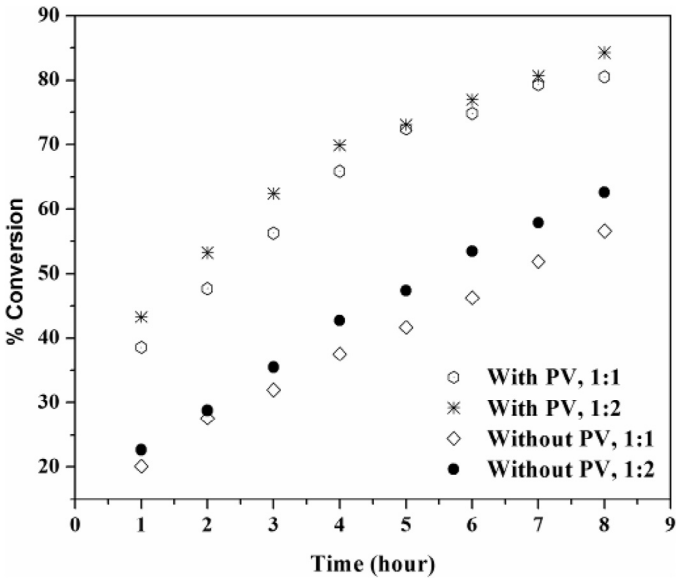

Fig. 4. Effect of molar ratio of acid to alcohol on the conversion of propionic acid for the esterification with PV and without PV.

pervaporation experiments, the operating parameter namely effective membrane surface area to initial reaction volume (S/V) was also studied in addtion to other three parameters viz, catalyst loading, initial molar ratio of acid to alcohol and reaction temperature to evaluate the performance of the pervaporation assisted esterification reaction.

3.1. Effect of catalyst loading

The experiments were conducted at a temperature of 363 K and molar ratio of acid to alcohol of 1:2. The effect of catalyst loading was investigated by varying the catalyst amount from 1% to 3% wt/wt. The results obtained after running the without and with PV experiments are presented in Fig. 3. As can be seen from Fig. 3, the increasing amount of catalyst favours the formation of ester. For the experiments without PV the conversion of propionic acid reached up to 65.17% for the catalyst loading of 3 wt% for the reaction time of 8 h. However, the enhanced conversion of 89.82% was observed for experiments coupled with pervaporation with similar operating conditions. These enhanced conversions observed in pervaporation coupled experiments were due to the equilibrium shift caused by PVA–PES membrane [17]. The equilibrium shift was caused by the permeation of water through the hydrophilic membrane.

3.2. Effect of molar ratio

It is a well known fact that the large excess of one reactant, generally alcohol, causes the increased conversions [18]. The effect of molar ratio was investigated at a temperature of 363 K and catalyst loading of 1% (wt/wt). The initial molar ratio of propionic acid to isobutyl alchol was varied from 1:1 to 1:2 and the results are shown in Fig. 4. As can be seen from Fig. 4, the conversion of propionic acid increased with increase in molar ratio. However, the difference in conversion of propionic acid was observed for batch and pervaporation experiments. The conversions of 56.61% and 62.58% were observed for the molar ratios of 1:1 and 1:2 respectively for the reaction time of 8 h for the batch experiments, whereas the conversions of 80.54% and 84.26% were achieved for molar ratios of 1:1 and 1:2 respectively for the pervaporation coupled experiments with similar operating conditions. This can be attributed to the fact that the increased alcohol concentrations shift the equilibrium to forward direction which in turn causes more water formation. Subsequently, the membrane will permeate this formed water which would result in enhacement in conversion.

3.3. Effect of temperature

The esterification of propionic acid and isobutyl alcohol was performed for both with PV and without PV experiments at a molar ratio of 1:2 and catalyst loading of 1% (wt/wt). The experiments were performed by varying the temperature from 343 to 363 K. Fig. 5 indicates the effect of temperature on the conversion of propionic acid for both with PV and without PV experiments. It is evident from Fig. 5 that the conversion of propionic acid increases with increase in temperature. For the experiments without PV, the conversions reached up to 53.61% and 62.58% for the temperatures of 343 K and 363 K respectively for the reaction time of 8 h. However, the conversion of propionic acid for the experiments with PV reached up to 76.54% and 84.26% at temperatures of 343 K and 363 K respectively with similar operating conditions. Due to the removal of water from the reaction mixture, higher conversion of propionic acid was achieved with pervaporation coupled esterification.

3.4. Effect of S/V ratio

The ratio of effective membrane area to initial reaction volume (S/V) is one of the most essential factors of pervaporation assisted process. The effect of the ratio of effective membrane area to initial reaction volume on the conversion

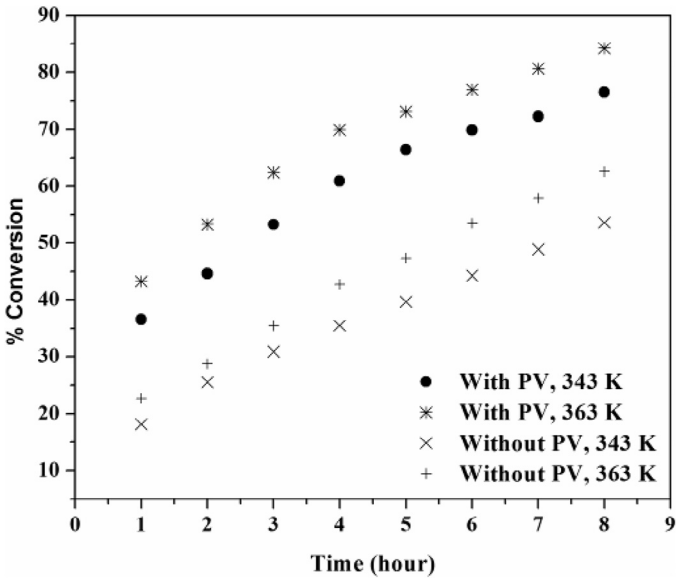

Fig. 5. Effect of temperature on the conversion of propionic acid for the esterification with PV and without PV.

of propionic acid was investigated by performing experiments at a temperature of 363 K, molar ratio of 1:2 and catalyst loading of 1% (wt/wt) by varying (S/V) ratio as 51.66, 38.75, and 31 m^{-1}. Since the membrane area is constant throughout the process, the S/V ratio was varied by varying the total reaction volume. The results are shown in Fig. 6. As can be seen from Fig. 6, the conversion of propionic acid decreased with decrease in (S/V) ratio. The conversion of propionic acid was obtained as 84.26%, 76.69%, and 72.22% for S/V ratios of 51.66, 38.75, and 31 m^{-1} respectively for the reaction time of 8 h. This elucidates that the higher intial reaction volume brings the lower esterification conversion within the specified membrane area. This is due to the lower water removal through the membrane at

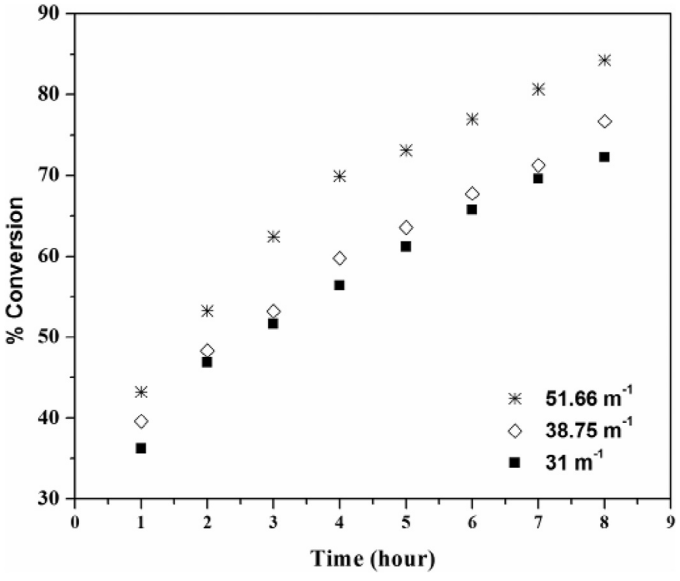

Fig. 6. Effect of S/V ratio on the conversion of propionic acid for the esterification with PV.

higher reaction volume. This concludes that higher S/V ratio favors the enhancement of esterification reaction. In pervaporation assisted process, the low membrane permeability can be prevailed over by employing the larger membrane area [19].

4. Conclusions

The present study deals with the comparison between batch and pervaporation assisted esterification of propionic acid and isobutyl alcohol to produce isbutyl propionate and water using *p*-TSA as a catalyst. The effects of process parameters such as catalyst loading, molar ratio of acid to alcohol, reaction temperature and ratio of effective membrane area to intial reaction volume (S/V) were investigated. The pervaporation assisted esterification gave the better conversion than the batch esterification. Moreover, the ester conversion was enhanced by increasing the process parameters such as, catalyst amount, molar ratio of acid to alcohol, reaction temperature and S/V ratio. The polymeric hydrophilic PVA–PES membrane which was used in the pervaporation experiments showed a high selectivilty towards the water removal. Thus, the coupling of pervaporation was proven to be an efficient method for enhancing the conversion of esterification reaction.

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